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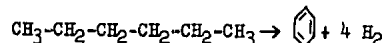
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THE MECHANISM OF CATALYTIC DEHYDROCYCLIZATION OF PARAFFIN HYDROCARBONS

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Fifteen years ago, USSR scientists (1) discovered the catalytic dehydrocyclization reaction of paraffin hydrocarbons, in which aromatic hydrocarbons are formed. For example, benzene is formed from hexane as the result of the formation of a six-member ring and subsequent dehydrogenation, viz:



while toluene is obtained from heptane, etc. The dehydrocyclization reaction has been subjected to detailed investigation by USSR and foreign scientists, and as a result of these investigations, the aromatization of paraffin hydrocarbons has found application on an industrial scale.

The mechanism of processes involved in catalytic dehydrocyclization has not yet been clarified completely.

The opinions of B. A. Kazanskiy and A. F. Plate on the mechanism of dehydrocyclization are stated in a number of articles and in A. F. Plate's book. According to these ideas (2), based on the multiplet theory of catalysis, groups of six atoms in regular hexagons consisting both of metal atoms and oxygen atoms exist on the surface of a catalyst which consists of sesquioxides, such as chromium, aluminum, or vanadium oxides. The symmetry of these sextets corresponds to the symmetry of the six-membered benzene ring. On platinum (3) there is also sextet adsorption of hydrocarbons (in plane III) which permits superimposition of the hydrocarbons in the form of hexagons (on the role of the sextet of metal atoms in the reaction of opening the five-member ring on platinum catalysts, cf. the report by B. A. Kazanskiy). (4) When the straight-chain paraffin hydrocarbon is on the surface of the catalyst, the sextet of atoms on the surface acts on the hydrocarbon molecule in such a way that the

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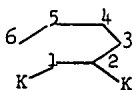
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carbon atom of this molecule will be oriented, under the influence of the atoms of the catalyst, symmetrically to the surface in the form of a flat adsorbed hexagon capable of forming a ring which is similar to cyclohexane and its derivatives. It seems to us that this hypothesis has no real physical foundation.

E. Herington and E. K. Rideal (5) start out from another idea. They suggest that the first act in the chain of processes of dehydrocyclization is the simultaneous splitting off of pairs of hydrogen atoms from the paraffin hydrocarbon molecules and the formation from it of an olefin, for instance formation of hexene from hexane. The hexene molecule, adsorbed at the point of the double bond and bound to two atoms of the catalyst, can form a ring only if it is oriented in such a manner that chemisorption takes place at the points C_1-C_2 or C_5-C_6 as result of the migration of the double bond.



K = catalyst

The assumption that the first act of the cyclization reaction of paraffin is the dehydrogenation of the molecule into an olefin has no sound basis. Nevertheless, the idea that olefins play an essential part in the process may be justified by the fact that their cyclization is much easier to carry out than that of paraffins.

Actually, on an active chromium-aluminum catalyst prepared by a special method, we obtained the results cited in the appended table.

In the intervals between the experiments, the catalyst was regenerated by passing air over it to burn out the polymers which had deposited. The higher the reaction temperature and the more olefins are contained in the original mixture, the greater is the quantity of polymers that form and are deposited.

The appended table shows that the conversion of heptane into aromatic hydrocarbon on one contact with the catalyst amounts to 31.2 mol percent. Starting with pure heptene, we obtained, under exactly the same conditions, a conversion into aromatics amounting to 52.5 percent, despite the fact that part of the heptene was turned into resin. Mixtures of the heptane and heptene gave yields somewhere between the above figures.

On analyzing the possible mechanism of cyclization and using experimental data on isotope exchange of hydrogen in paraffin and olefin hydrocarbons as a basis, we arrived at the following viewpoint.

Chemisorption of paraffin and formation of adsorption radicals are indispensable for cyclization of paraffin hydrocarbons into six-member rings. The adsorbed hydrocarbon radicals are attached to the catalyst by a single bond C-K (K is the catalyst) and turned into space at different angles. Because of the limited capacity for rotation around the C-C bond, a change of the configuration of the hydrocarbon radical can take place, giving it various orientations in space. It may occur that the sixth carbon atom from the fixed carbon atom will be at such a distance from the surface of the catalyst that chemical interaction with the surface can take place. A geometrically correct controlling sextet of catalyst atoms is not required. The speed of cyclization will depend on the number of favorable orientations of the adsorbed radicals.

The adsorbed radical, fixed to the catalyst at the point C_1-K , can undergo not only cyclization, but can, at the same time, be dehydrogenated to an olefin as a result of a contact established between the neighboring carbon atom C_2 and the catalyst.

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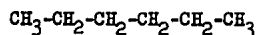
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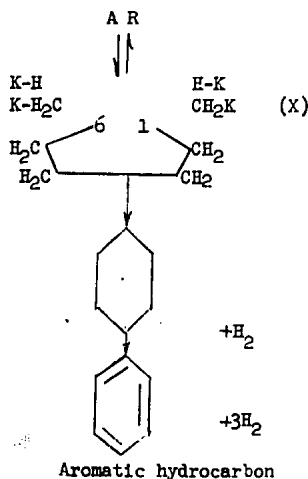
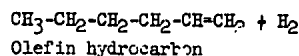
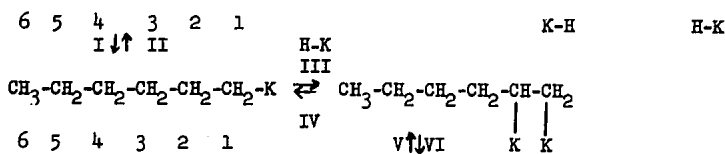
The process of transformation of the adsorbed radical into an adsorbed olefin can take place quickly and easily, and the reverse process can be just as fast. In the long run, these two processes will favor an increase in the number of orientations which are helpful to cyclization. The attendant process of dehydrogenation into olefin, or the introduction of ready-made olefin into the system, are of great importance in this conversion.

We propose the following scheme for the dehydrocyclization of n-hexane:

Paraffin hydrocarbon:



Dehydrogenation without cyclization



Cyclization under dehydrogenation

K = Catalyst
AR = Adsorbed Radical

An essential condition of cyclization is the process of formation of the adsorption radical AR. The criterion for the formation of radicals of various types, in particular AR, is the comparatively quick exchange of D and H atoms in the paraffin hydrocarbon molecule. On chrome-aluminum catalyst, heat-treated at 500°C, we could measure the rate of exchange between hydrogen and deuterium already at 300°C and with a contact time of 7 sec. Below that temperature and contact time, the rate of exchange is insignificant.

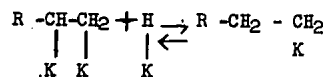
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As the result of the formation of an adsorption radical, chemisorption of AR with the adjacent atom C₂ (cf. scheme) and dehydrogenation quickly take place, limited by the equilibrium condition of the reaction $C_7H_{16} \rightleftharpoons C_7H_{14} + H_2$. The reverse process IV again leads to the formation of an adsorbed radical from the chemisorbed olefin and hydrogen:



The greater speed of processes III and IV as compared to process I guarantees formation per unit of time of a large number of radical orientations favoring cyclization. These radicals are connected to the catalyst by one C-K bond. Cyclization of the AR is possible even in the absence of olefines but as the number of favorable orientations is insufficient, it will take place on a smaller scale. The limit of the favorable orientation leading to the fixing of the sixth carbon atom C₆ on the surface is indicated in the scheme by (x).

The speed of the exchange of H for D in the olefin molecule may serve as an indicator for the ease with which reaction IV will proceed. According to our findings, exchange of H for D in olefin proceeds easily on heat-treated chrome-aluminum catalyst below 200°C. The ratio of the velocities of isotope exchange reactions in olefins and paraffins may serve as an indirect criterion for the increase in the number of favorable configurations of adsorption radicals which facilitate cyclization.

For estimating the probable ratio of yields of aromatics from various paraffin hydrocarbons, the procedure of Herington and Rideal (5) may be used, but it is necessary to start with the assumption of cyclization of a radical adsorbed at one carbon atom. The probability of the formation of six-member rings should be related not to the number of C-C bonds in the molecule of the original hydrocarbon, as is done by the two above authors, but to the number of carbon atoms.

Aromatization of Pentane- Pentene Mixtures

Temp 484°C, Catalyst Cr₂O₃ - K₂O - Al₂O₃ (Vol 10 ml)

Initial Mixture (mol %)		Mixture Passed Through Catalyst (ml/hr)	Yield of Liquid Products		Yield in mol % Obtained From the Mixture Passed Through:		
C ₇ H ₁₆	C ₇ H ₁₄		Weight %	N _d ²⁰	Olefins	Aromatics	Paraffins
100.0	0.0	4.15	88	1.4215	12.3	37.2	48.0
90.7	9.3	3.60	86	1.4290	13.3	36.6	34.8
76.9	23.1	3.98	77	1.4255	14.1	34.3	32.7
64.6	35.4	3.85	77	1.4338	13.1	37.0	30.6
42.5	57.5	3.92	77	1.4388	15.3	42.8	22.2
13.5	86.5	4.0	73	1.4478	17.4	46.8	12.0
13.5	86.5	3.90	73	1.4465	13.2	47.5	14.9
0.0	100.0	4.03	70	1.4566	18.8	52.5	4.2

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